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Testing of Space-Survivable POSS (Polyhedral Oligomeric Silsesquioxane) Polyimides"

SYNTHESIS AND ATOMIC OXYGEN EROSION TESTING OF SPACE-SURVIVABLE POSS (POLYHEDRAL OLIGOMERIC SILSESQUIOXANE) POLYIMIDES

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ABSTRACT

This paper presents several characterization studies of the surfaces of newly synthesized POSS-containing polyimides before and after exposure to atomic oxygen (AO). AO exposure testing was conducted independently at the University of Florida and Montana State University revealing comparable data. The exposed surfaces were characterized using X-ray photoelectron spectroscopy, and atomic oxygen erosion rates were calculated using stylus surface profilometry. The data indicate that AO induced erosion of polyimides containing POSS is drastically reduced as a result of a passivating silica layer is formed on the surface of the polymer.

1. INTRODUCTION

Polyimides such as Kapton, are used extensively on spacecraft primarily as flexible substrates for lightweight, high-power solar arrays because of their inherent strength, temperature stability, excellent insulation properties, UV stability and IR transparency. They are also used in conjunction with Teflon FEP as the outer layer of multi-layer thermal control insulation because of their superior optical properties, including low solar absorptance and high thermal reflectance. In these multilayer insulations a metalized layer is typically applied to the backside in order to reflect incident sunlight. In addition, polyimides are the predominant materials used to build space inflatable structures.

However, over the last twenty years, it has been well established through space-based experiments and ground simulations that polymeric materials and films, undergo severe degradation as a result of the aggressive environment encountered in low Earth orbits (LEO). In this high vacuum environment, materials are subjected to the full spectrum of solar radiation and must endure constant thermal cycling and bombardment by low and high-energy charged particles as well as high incident fluxes of AO. These harsh conditions combined with the need for lighter weight and lower cost man-made orbiting bodies necessitates the design of multi-functional, space-survivable materials.

Hybrid inorganic/organic polymers have the potential to meet the requirements of space-survivable materials by bridging the gap between ceramics and plastics, resulting in the prevention of AO and radiation damage that has hampered the widespread application of organic polymers in space. The Polymer Working Group at the Air Force Research Laboratory at Edwards AFB has incorporated inorganic POSS (Polyhedral Oligomeric Silsesquioxane) frameworks into traditional polymer systems resulting in hybrid POSS-polymers with dramatic property enhancements [1-3]. POSS frameworks (Fig. 1) are comprised of a three dimensional inorganic cage structure with a 2:3 Si:O ratio, surrounded by tailorable organic groups [4-6].

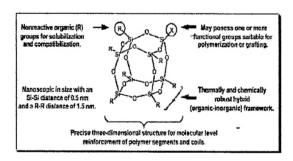


Fig. 1. Anatomy of a POSS nanostructure

They are functionalized monomers that can be copolymerized, grafted and blended into traditional polymer systems [7]. The anatomy of a POSS molecule shown in Fig. 1 is defined by the following (1) Single molecules with dimensions ranging in size from 0.7 nm to 3 nm with an average of 1.5 nm rendering them approximately two orders of magnitude smaller than conventional inorganic fillers (quartz talc ~ 100 μm, fumed Si ~100 nm, colloidal $SiO_2 \sim 10$ nm). (2) A thermally and chemically robust inorganic framework with well defined threedimensional polyhedral geometries. (3) One or more functional groups which enable grafting and copolymeriztion. (4) Nonreactive R groups (cyclopentyl, cyclohexyl, phenyl, isobutyl, methyl) which aid in the compatibilization with the polymer matrix [3,7]. Addition of these POSS nanostructured frameworks into polymers results in increased use and

decomposition temperatures, improved mechanical properties, and oxidation resistance.

Our previous research has shown that chemical manipulation of the unreactive organic groups surrounding the POSS cage [3,7] enables dispersion of POSS nanostructures throughout the polymer matrix at high POSS loadings via blending and copolymerization techniques [1,2,7]. We have also shown that polymers containing POSS rapidly form a ceramic-like, passivating and self-healing silica layer when exposed to high incident fluxes of AO [8-10]. We believe that this self-healing nature is a direct result of POSS compatibility and dispersion throughout the polymer matrix. If the glassy silica layer erodes or suffers a microdefect, it would quickly reform due to the uniform POSS dispersion.

This paper presents a characterization study of the surfaces of newly synthesized POSS-containing polyimides before and after exposure to AO. Atomic oxygen exposure testing was conducted independently at the University of Florida and Montana Sate University revealing comparable data. The exposed surfaces were characterized using X-ray photoelectron spectroscopy, and atomic oxygen erosion rates were calculated using stylus surface profilometry. Changes in the surface topography were measured using atomic force microscopy.

2. RESULTS AND DISCUSSION

2.1 Synthesis of POSS Polyimide Copolymers

A POSS framework 1 with two anilino pendant groups was provided by Prof. Frank Feher and prepared as described in [11]. Using this monomer, various POSS-polyimide random copolymers were synthesized as shown in Fig. 2 with POSS loadings corresponding to 0, 5, 10 and 20 wt%.

2.2 Thermo-mechanical Properties of POSS-Polyimides

The linear viscoelastic properties of polyimides with differing amounts of POSS incorporation were determined using a dynamical mechanical analyzer in tensile mode over a wide range of temperatures. Fig. 3 presents a comparison of storage modulus, E'(T), as a function of temperature for polyimides with 0 wt%, 5 wt%, and 10 wt% POSS segments, respectively. All polymers exhibited a mechanical relaxation transition at temperature near 400 °C indicating the onset of large scale thermally induced motions. It is well known that this type of polyimide, Kapton, does not flow at elevated temperature. This was confirmed by the change in the magnitude of E'(T) at the transition temperature, i.e., from around 1 GPa to 100 MPa. Normal (flexible) polymers would have dropped down to about 1 MPa. As shown in Fig. 3, at temperatures below this relaxation, the magnitude of E'(T) was not significantly affected by the addition of POSS segments in the polymer chain. However, at temperatures above this relaxation, the magnitude of E'(T) increases as the amount of POSS segments in the polymer chain increases.

Fig. 2. Synthesis of POSS-Polyimides

The corresponding value of the plateau moduli depends on the amount of POSS incorporation in the polymer. The appearance of these plateaus at temperatures above the mechanical relaxation transition indicate a very strong POSS-POSS interaction where the modulus of polymer was not affected by the change in temperature. These observations suggest that POSS-POSS interactions reduce the motion of the polymer chains and add mechanical strength to these polymer systems above the glass transition in a manner that could be analogous to entanglements.

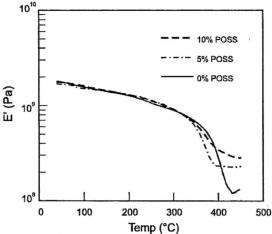


Fig. 3 Plot of storage modulus E'(T) vs. temperature for Kapton and POSS-Kapton polymers

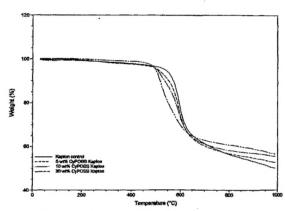


Fig. 4. TGA for Kapton and POSS-Kapton polyimides under N₂, 10 °C/min heat ramp

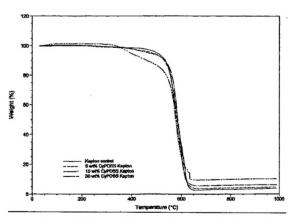


Fig. 5. TGA for Kapton and POSS-Kapton polyimides under air, 10 °C/min heat ramp

Fig. 4 and Fig. 5 show thermal gravimetric analysis (TGA) charts of Kapton control and 5, 10 and 30 wt% POSS-polyimides under nitrogen and air purge respectively. As can be seen from Fig. 4, the onset of thermal degradation under a nitrogen atmosphere for

the POSS containing polyimides begins at decreasing temperatures with increasing POSS content.

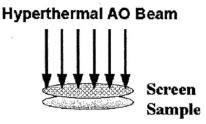


Fig. 6. AO etching experiment using a protective screen to shield selective areas of the sample for profilometry measurements

2.3 Profilometry and Atomic Oxygen Etching Experiments

Samples of POSS-Polyimide films underwent a series of AO etching experiments where they were exposed to an hyperthermal O-atom beam produced by a 7 Joule-pulsed CO₂ laser source. This AO source has been well characterized and described previously [12]. The resultant beam consists predominantly of fast neutrals, with a very small ionic fraction (<10⁴). Average kinetic energies of the fast species in the beam can range from 2 to 15 eV.

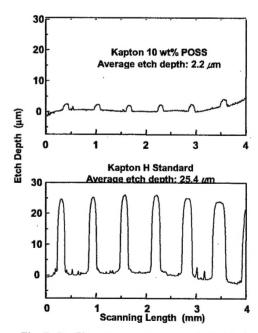


Fig. 7. Profilometry measurements obtained after a total AO fluence of 8.47 x 10²⁰ atoms/cm², equivalent to an approximate 10 day simulated LEO dosage

As depicted in Fig. 6, a protective screen was placed in-between the sample and beam path in order to

selectively erode only certain portions of the samples. The difference in etch depth between the eroded and protected part of the samples was then measured using stylus surface profilometry. Surface profilometry is a technique in which a diamond stylus, in contact with a sample, can measure minute physical surface variations as a function of position. It is commonly used to measure film thickness in thin film deposition and processing. By measuring the difference in height between the etched and unetched portions of the polymer sample, it is possible to calculate an AO reaction efficiency (Rc) or erosion rate for the material for a given flux. Profilometry measurements for the Kapton H standard and a 10 wt% POSS-Kapton polyimide sample are shown in Fig. 7 after a total fluence of 8.47 x 10²⁰ atoms/cm². This corresponds to 100,000 pulses of the laser atom source and correlates to an approximate 10 day simulated LEO dosage.

These measurements reveal that the average etch depth for the Kapton HN standard was 24.5 microns which corresponds to a calculated $R_{\rm c}$ of 3.00 x 10^{-24} cm³/atom. This value agrees with previously reported erosion rates based on space flown and ground tested Kapton samples [13]. However, under the same conditions, the 10 wt% POSS-Kapton polyimide etched on average only 2.2 microns corresponding to an $R_{\rm c}$ of 2.56 x 10^{-25} cm³/atom. It is interesting to note that this full order of magnitude improvement in atomic oxygen reaction efficiency is brought about by only a 10 wt % (approximately 1 mole%) addition of POSS copolymerized in the polymer matrix.

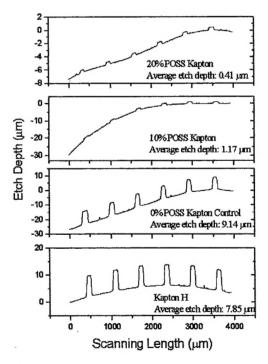


Fig. 8. Profilometry measurements obtained after a total AO fluence of 2.62 x 10²⁰ atoms/cm², equivalent to an approximate simulated 3 day LEO dosage

The experiment was repeated for a smaller AO fluence of 2.62 x 10²⁰ atoms/cm² exposing a commercially available Kapton H standard, a Kapton control sample with no POSS and a 10 and 20 wt% POSS-Kapton sample. Fig. 8 shows a multiplot of the profilometry measurements of these samples. The data for these plots reveal a decreasing average etch depth and corresponding atomic oxygen reaction efficiency as the POSS content in the polymer increases. Again, a full order magnitude improvement in the atomic oxygen reaction efficiency is obtained from addition of 10 wt% POSS, while addition of 20 wt% POSS improves the reaction efficiency by 22.5 times.

The superior performance of polyimides containing POSS is further highlighted by atomic force microscopy images before and after exposure to AO as shown in Fig. 10 and Fig. 11. These images reveal that the surface roughness increases dramatically for the Kapton control sample after AO exposure from 1.09 to 102 nm. In contrast, the surface roughness of the Kapton polyimides with POSS only slightly increases from 1.03 to 17.7 nm and from 1.55 to 6.75 nm for the 10 wt% and 20 wt% POSS respectively.

The protection provided to polyimides that contain POSS is actually much greater when looking at much longer exposure times. As can be seen in Fig. 9, erosion of the 10 and 20wt % POSS Kaptons to 400,000 AO beam pulses is drastically less than that of the Kapton control sample. This suggests that there is a equilibrium point where the surface is nearly completely protected from further AO attack resulting in negligible erosion. This is a result of the passivating and self-healing silica layer that is formed as a result of the nanodisperesed POSS moieties reacting with AO. This surface layer was characterized using X-ray photoelectron spectroscopy (XPS) as described below prevents further degradation of the underlying polymer.

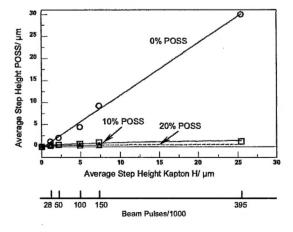


Figure 10. Erosion of Kapton and POSS Kapton versus AO beam pulses

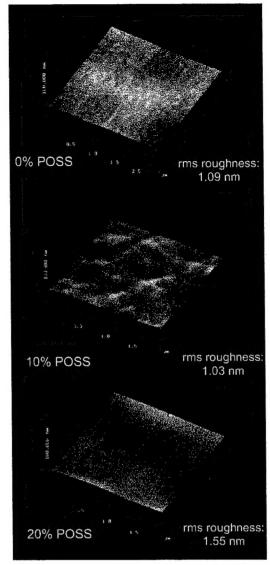


Fig. 10. Atomic Force Microscopy images of Kapton control and 10 and 20 wt% before exposure to AO

2.4 In-situ XPS Analysis After Exposure to an ESD Atomic Oxygen Source

A 10 wt% POSS-Polyimide film has been characterized in situ by using XPS before and after incremental exposures to the flux produced by an electron stimulated desorption (ESD) atomic oxygen source. This source, developed by Hoflund and Weaver [14], is ultrahigh vacuum (UHV) compatible, operates with the sample at room temperature and produces a high purity, hyperthermal AO flux with an O atom: O' ratio of ~108.

XPS spectra were first obtained from the as-entered, solvent-cleaned sample. The sample was then transferred into an adjoining UHV chamber that houses

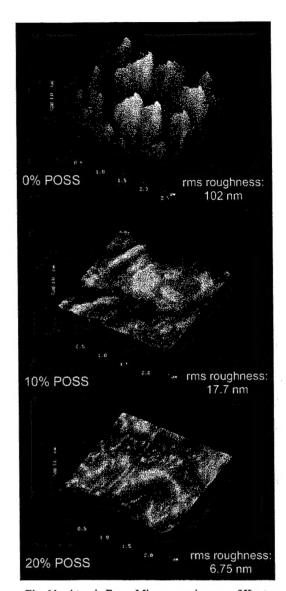


Fig. 11. Atomic Force Microscopy images of Kapton control and 10 and 20 wt% after a total AO fluence of 8.47 x 10²⁰ atoms/cm², equivalent to an approximate 10 day simulated LEO dosage

the atomic oxygen source via a magnetically coupled rotary/linear manipulator. There the surface was exposed to a hyperthermal AO flux and re-examined without air exposure after total exposure times of 2, 24, and 40 h. The approximate normal distance between the sample faces and source in this study was 15 cm, at which distance the flux was about 2.0 x 10¹⁵ atoms/cm²-s for the instrument settings used. The sample was maintained at room temperature during the AO exposures with a slight temperature increase to 50°C due to exposure to the X-ray source during XPS data collection. The substrate temperature was determined using a chromel-alumel thermocouple. After the 40 h AO exposure, the sample was exposed

to air (room temperature, ~22°C, relative humidity ~60%) and again examined using XPS.

Fig. 12 Molecular structure of POSS-Kapton with numerically labeled atomic sites

The POSS-Kapton molecular structure with labeled atomic sites is shown in Fig. 12. XPS survey spectra obtained from a solvent-wiped 10 wt% POSSpolyimide surface before and after the 2, 24 and 40 h AO exposures and final air exposure are shown in Fig. 13. The peak assignments shown in Figure pertain to all five spectra. The predominant peaks apparent in these spectra include the C 1s, N 1s, O 1s, Si 2p, Si 2s, O 2s and O Auger peaks. Significant changes in relative peak heights are observed for the C, O, and Si features following the O-atom exposures. XPS is a surface sensitive technique ideally suited for studying AO erosion of spacecraft materials. The outermost surface region which is affected to the greatest extent due to reaction with AO also makes the largest contribution to the XPS signal. The weighted average compositional values of the near-surface region determined using the homogeneous assumption are shown in Table 1 as a function of AO fluence. They provide a trend which is indicative of the chemical alterations occurring during AO exposure. This trend is supported by the chemical state alterations determined by XPS, which are discussed below.

Table 1. Near-surface composition determined from XPS data obtained from the as-entered, AO and airexposed 10 wt% POSS-Polyimide sample

Surface sample treatment	AO fluence O/cm ²	o C	omposi Si	tion, at.9	% N	O:Si ratio
As entered		15,9	4.6	74.5	4.9	3.4
2 h r AO	1.44×10 ¹⁷	14.3	4.9	72.6	8.2	2.9
24 h AO	1.77×10 ¹⁸	11.1	4.4	79.6	4.9	2.5
40 h AO	4.53×10 ¹⁸	9.1	3.7	81.5	5.6	2.4
Air exposed	4.53×10 ¹⁸	13.9	3.5	76.8	5.8	3.9

As can be seen in Fig. 13, the O 1s peak decreases significantly upon exposure to the AO beam. As a result, the O/Si atomic ratio of 3.4 for the as-entered sample, decreases gradually to 2.4 after the 40 h AO exposure. This reduction of the O/Si ratio is due to AO induced surface compositional changes resulting in the removal of carbonyl groups from the polymer chain and formation of a surface silica layer as shall be explained in the high resolution spectra that follow. After exposure to air, the O/Si atomic ratio increases to 3.9 corresponding to adsorption of species present in

air. An overall increase is observed in the C concentration on the surface during increased exposure. Since the surface compositions presented in Table 1 are relative, it is expected that as the O concentration decreases the C and Si would increase.

High-resolution XPS C 1s, O 1s, N 1s and Si 2p spectra obtained from the as-received, solvent-wiped surface before and after the 2, 24 and 40 h O-atom exposures are shown in (a)-(d) of Fig. 14 through Fig. 17. Spectra (e) of these figures were obtained after the exposure to air following the 40 h AO exposure. Variations in peak shapes and positions are observed between the nonexposed, AO-exposed, and air-exposed surfaces, indicating that the chemical species distribution is altered by exposure to the AO flux and then to air. In addition, no surface charging of the sample was evident during the experiment as this would have altered the spectra resulting in a significant binding energy (BE) shift. Differential charging would have resulted in peak broadening or peak multiplicity, however, this was not observed in this study.

10 wt% POSS Kapton Polyimide

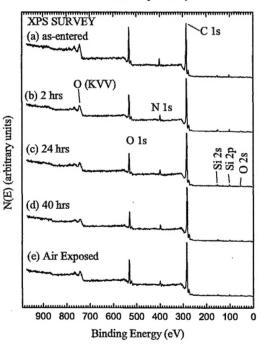


Fig. 13. XPS survey spectra obtained from a 10 wt% POSS-polyimide film as entered (a), after 2 h (b), 24 h (c), and 40 h exposure to the hyperthermal AO flux (d), and air exposure after the 40 h exposure (e)

The C 1s peak for the as entered sample in Fig. 14 is broad and centered at 284.7 eV indicating the predominant form of carbon present is aromatic. A high binding energy shoulder is present at 288.6 eV corresponding to the carbonyl carbon (6) in Fig. 12. However, as is also observed Kapton, this shoulder

diminishes upon exposure to AO. This is due to erosion of the carbonyl groups from the polymer backbone. This also results in a chemical state change of nitrogen on the surface as observed in the N 1s spectra in Fig 16.

The N 1s spectrum for the as entered sample is centered at 400.6 eV, corresponding to nitrogen bound as an imide functional group. However, as with regular Kapton, as the N-C=O bonds are broken upon removal of the carbonyl groups to form CO and CO₂, a lower binding energy shoulder begins to emerge in the N 1s spectra.

The chemical state changes in carbon and nitrogen associated with erosion also coincide with chemical state changes in the O 1s and Si 2p spectra in Fig. 16 and Fig. 17, which as with other POSS-polymers, reveal the formation of a silica layer on the outer surface. Upon inspection, it is evident from these spectra that a transition occurs for oxygen and silicon from a lower binding energy corresponding to the silsesquioxane to a higher binding energy and oxidation state associated with the formation of SiO₂ on the surface. These surface changes are presumably responsible for the reduced erosion rates and improved AO reaction efficiencies discussed presented herein.



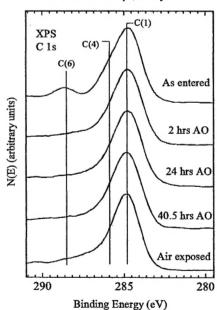


Fig. 14. XPS C 1s spectra obtained from a 10 wt% POSS-polyimide film as entered (a), after 2 h (b), 24 h (c), and 40 h exposure to the hyperthermal AO flux (d), and air exposure after the 40 h exposure (e)

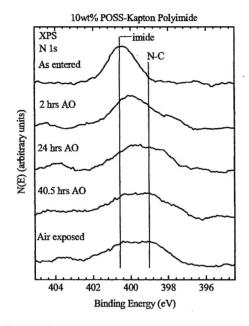


Fig. 15. XPS N 1s spectra obtained from a 10 wt% POSS-polyimide film as entered (a), after 2 h (b), 24 h (c), and 40 h exposure to the hyperthermal AO flux (d), and air exposure after the 40 h exposure (e)

10wt% POSS-Kapton Polyimide

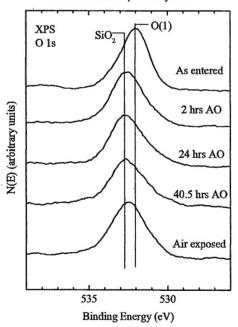


Fig 16. XPS O 1s spectra obtained from a 10 wt% POSS-polyimide as entered (a), after 2 h (b), 24 h (c), and 40 h exposure to the hyperthermal AO flux (d), and air exposure after the 40 h exposure (e)

10wt% POSS-Kapton Polyimide

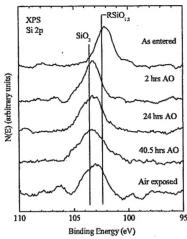


Fig. 17. XPS Si 2p spectra obtained from a 10 wt% POSS-polyimide film after insertion into the vacuum system (a), after 2 h (b), 24 h (c), and 40 h exposure to the hyperthermal AO flux (d), and air exposure after the 40 h exposure (e)

3. CONCLUDING REMARKS

The incorporation of POSS nanostructures into polyimides should significantly extend the usable lifetime of these materials in LEO applications. They exhibit a significantly improved oxidation resistance due to a rapidly formed ceramic-like, passivating and self-healing silica layer when exposed to high incident fluxes of atomic oxygen. The formed layer prevents further degradation of underlying virgin polymer. This technology could be easily adapted to other polymeric systems, such as structural polymers like polyethylene and polypropylene, revolutionizing the field of space-survivable materials

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Synthesis and Atomic Oxygen Erosion Testing of Space-Survivable POSS (Polyhedral Oligomeric Silsesquioxane) Polyimides



9th International Conference on Materials in a Space Environment Noordwijk, The Netherlands, 16-20 June 2003 Capt. Rene I. Gonzalez, Ph.D.
Project Leader
POSS-Polymer Working Group
Air Force Research Laboratory
(661)275-5252
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Approved for public release; distribution unlimited.

Polymeric Materials

- missions. (\$5,000 to \$10,000/1b to put Cost is the variable plaguing all space payload in orbit)
- Materials are one of the main drivers of cost for space missions.
- (lightweight, easy to process, versatility) Polymers offer many advantages
- However, polymers are subject to severe degradation in Low Earth Orbit space environment



(Altitudes of 200 to 1500 km) LEO Environment

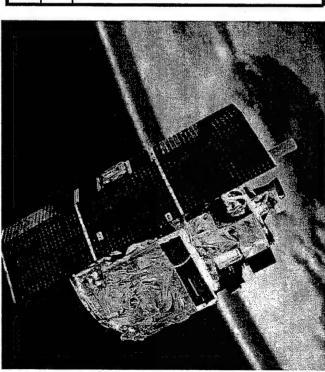


- Atomic Oxygen
- $\sim 10^8 \text{ atoms/cm}^3$
- Formed from photo-dissociation of O₂ in atmosphere.
- Actual flux on spacecraft traveling at 8 to 12 km/s ~10¹⁵ atoms/cm²•s
- collision energy \sim 5eV (C-C \sim 4 eV, C-N \sim 3 eV)
- Low-energy and high energy charged particles.
- Thermal cycling -50 to 150°C
- Solar UV and VUV radiation
- VUV wavelengths in LEO extend below 290nm.
- Bond scission and radical formation can lead to embrittlement.



Goal: Develop Multi-Functional, Space-Survivable Materials





Atomic Oxygen Reaction Efficiency cm ³ /atom	ction Efficiency	cm³/atom
Material	Rel. Rates⁺	LEO
Kapton	1	3.0×10^{-24}
Polyethylene	6.0	3.7×10^{-24}
FEP Teflon	<0.03	$<0.05 \times 10^{-24}$
FEP Teflon	9.0	1.0×10^{-24}
(Solar Max)		
Siloxane-imide block copolymers(25% /75%)	0.1	0.3 x 10 ⁻²⁴
Epoxy	9.0	1.7×10^{-24}

Satellites & Space Systems

Objectives

- Increase Space Survivability (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials
- Self-Passivating/Self-Rigidizing/Self-Healing based on Hybrid organic/ inorganic nanocomposite incorporation



60al: Develop Multi-Functional, Space-Survivable Materials



Bond	Dissociation Energy (EV)	չ (ոm)	Material
-C ₆ H ₄ -C(=O)-	3.9	320	Kapton®
O-N	3.2	390	Kapton®
CF ₃ -CF ₃	4.3	290	FEP Teflon®
CF ₂ -F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

Objectives

Satellites & Space Systems

- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials
- Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation



The state of the s

Develop High Performance Polymers that REDEFINE material properties

Ceramics HYBRID PROPERTIES

Use Temperature & Oxidation Resistance Toughness, Lightweight & Ease of Processing ·Hybrid plastics bridge the differences between ceramics and polymers



Polyhedral Oligomeric

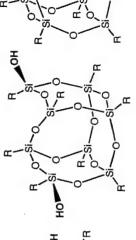


Silsesquioxanes

RSiX₃ acid or base hydrolysis

Blendables

Resin



Brown, Feher, AFRL, Hybrid Plastics



Polymer Working Group - Research



Basic R&D (6.1) PROGRAMS AFOSR

POSS Synthesis and Characterization POSS Polymer Processing POSS for Space-Survivable Materials

Applied R&D (6.2) PROGRAMS AFRL

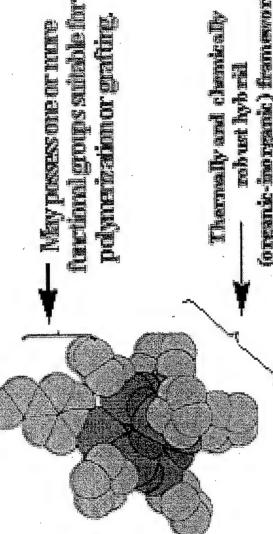
Solid Rocket Motor Insulation/Casing Liquid Rocket Engine Ducting High Temp Lubes/Jet Canopies/Radomes **Technology Transfer**





Nome a fire organic (M) granty s fort THE HEALTH

and a K. K. distance of 11.5 mm Manuscopie in sine will an



premis morganic) framework Themsily and clembally Table 17. Pall

tre se three dinengent ricucture for male uler boat reinforcement of polymer segments and colls.



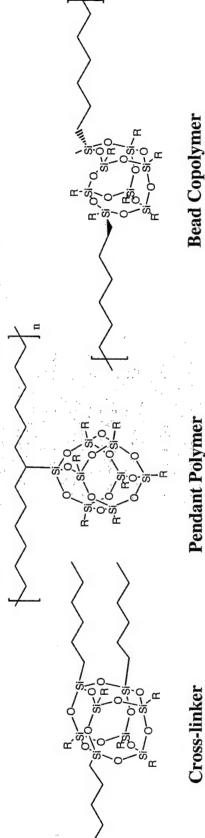
Why POSS and Why Nano?



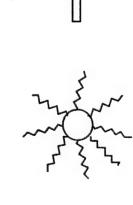
		Field	Property	Critical Length
		Electronics	Tunneling	1-100 nm
1 mm		Optical	Quantum Well	1-100 nm
Razor Blade Thickness	ickness		Wave Decay	10-1000 nm
		Polymers	Primary Structure	0.1-10 nm
100 µm — — — — — — — — — — — — — — — — — —		1	Secondary Structure	10-1000 nm
		Mechanics	Dislocation Interaction	1-1000 nm
10 um	-ibers		Crack Tip Radius	1-100 nm
			Entanglement Rad.	10-50 nm
1 µm—	ers &	Therm-Mech.	Chain Motion	0.5-50 nm
Polymer Morphology	hology	Nucleation	Defect	0.1-10 nm
· Viruses & Nanofillers	nofillers		Critical Nucleus Size	1-10 nm
10 nm —			Surface Corrugation	1-10 nm
• POSS® Building Blocks	Blocks	Catalysis	Surface Topology	1-10 nm
	S.	Biology	Cell Walls	1-100 nm
0.1 nm — 1 → Atoms / Small Molecules	Molecules	Membranes	Porosity Control	0.1-5 nm



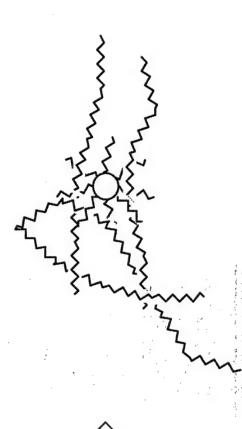
POSS Polymer Incorporation



Bead Copolymer



POSS Blending



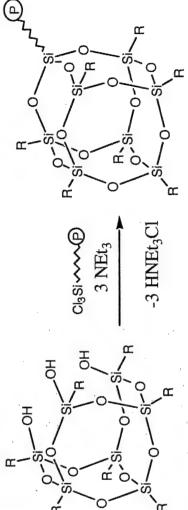


POSS Macromers For Nanocomposites



Cyclohexyl Phenyl O Cyclopentyl Ethyl IsoButyl

Completely New Polymer Feedstock Technology



Halides Nitriles
Alcohols Amines
Esters Isocyanates
Bisphenols Epoxides

Silanes Styryls Silanols a-olefins Silylchlorides Acrylics Norbornenyls

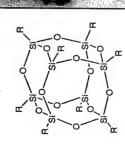
POSS technology is commercialized by Hybrid Plastics in Fountain Valley CA POSS-based macromers are available through either Gelest or Aldrich



compatibility with polymer matrix Affect Importance of R groups:



% POSS Blends in 2 Million MW



R = cyclopentyl

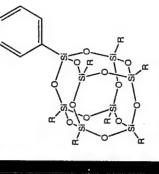




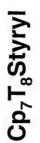
Domain Formation



Partial Compatibility



R = cyclopentyl





Phenethyl₈T₈



POSS Nanodispersion/Transparent Complete Compatibility-Immiscible POSS Crystallites



Polypropylene and Methyl₈T₈



POSS Drop Test Dr. R. Blanski Me8T8/i-PP

Fime Lapse 20X Б:<u>6</u>

Test Duration

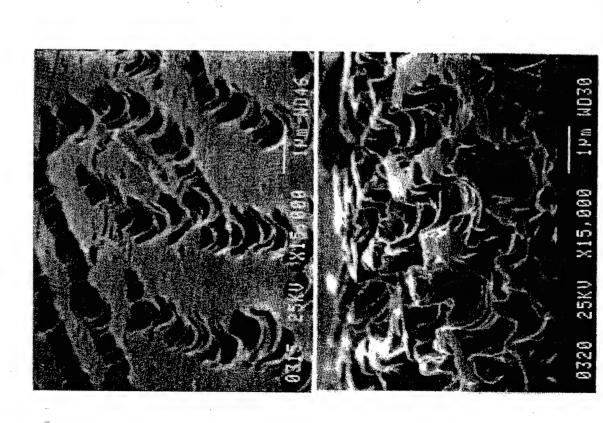


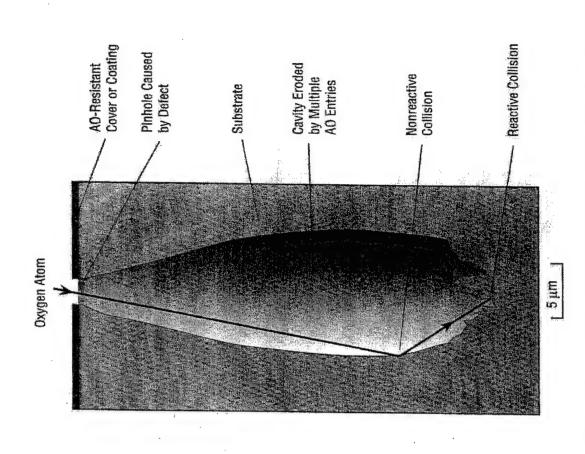
8 Feb 2001



- Test run at 190 °C
- 1 Kg weight
- 10% POSS gave a 28 % improvement

AO undercutting of LDEF Aluminized-Kapton Multilayer Insulation





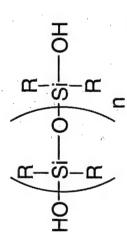
DeGroh, K.K., Banks, B.A., J. Spacecraft and Rockets, Vol. 31, No. 4, 656-664 (1994)

Siloxanes



High Si-O bond strength ~ 8 eV (C-C ~ 4 eV, C-N ~ 3 eV)

Oxyphilicity



$$R = CH_3$$

However, pure siloxane systems have

disadvantages

Chain Scission

Volatile cyclic species which recondense on

optical surfaces

Cyclo(Me₂SiO)₅

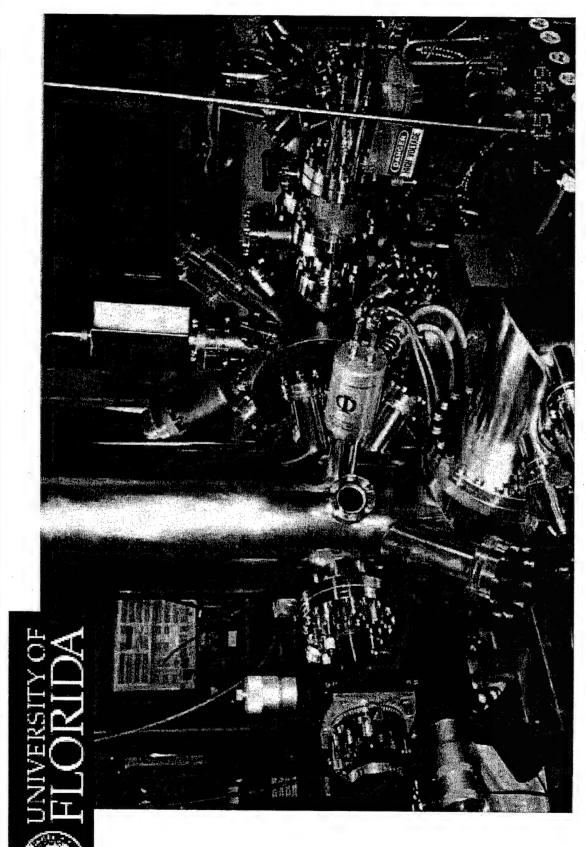
Cyclo(Me₂SiO)₆

Cyclo(Me₂SiO)₇

Cyclo(Me₂SiO)₃

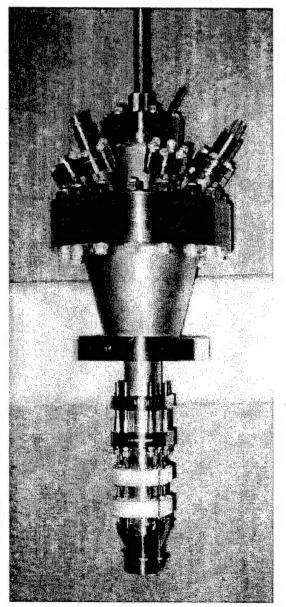
LEO Simulation Facility







Oxygen Atom Source

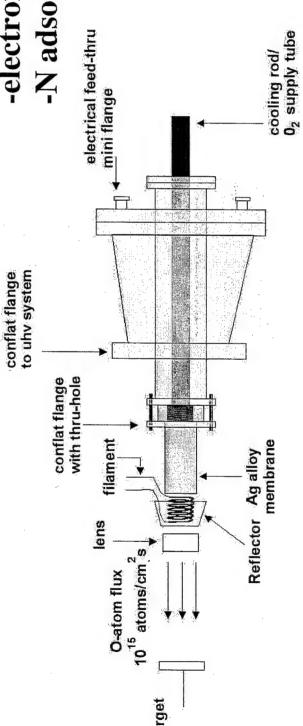


1. Adsorption -maximize pressure

2. Permeation-membrane thickness-temperature

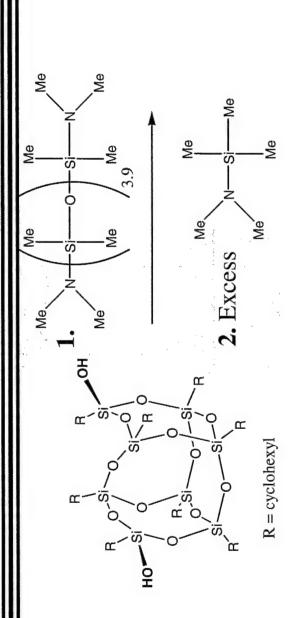
3. Desorption (ESD)
-electron current

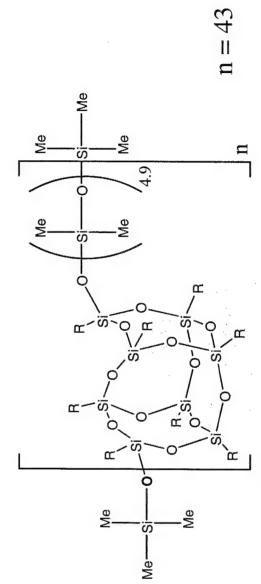
-N adsorbed neutrals



POSS-Siloxane

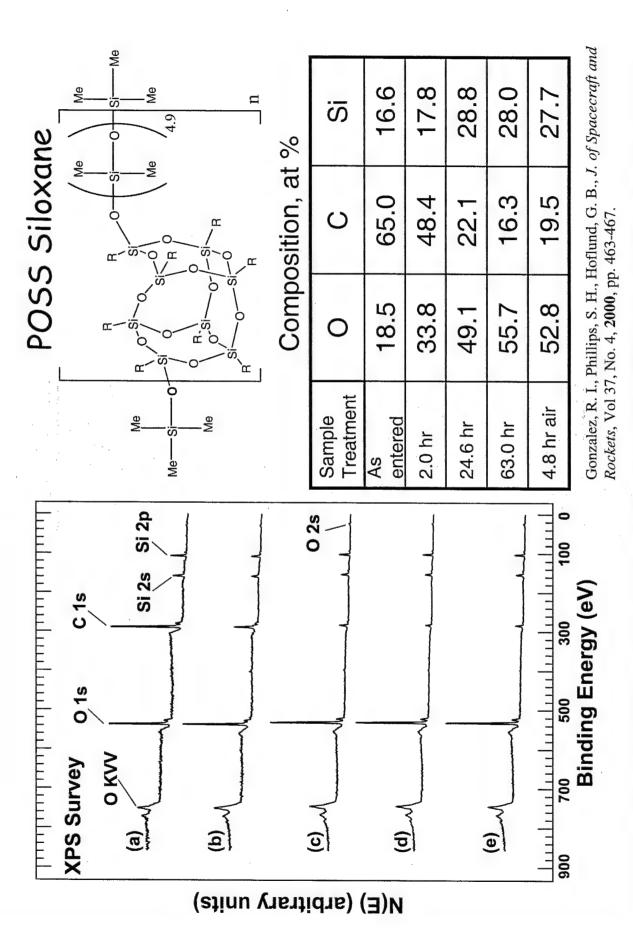




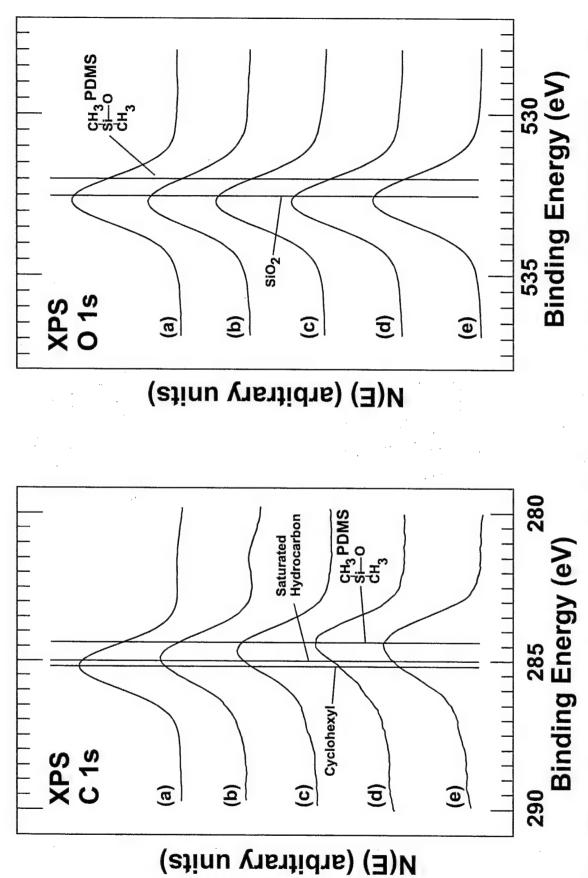


POSS-PDMS Copolymer

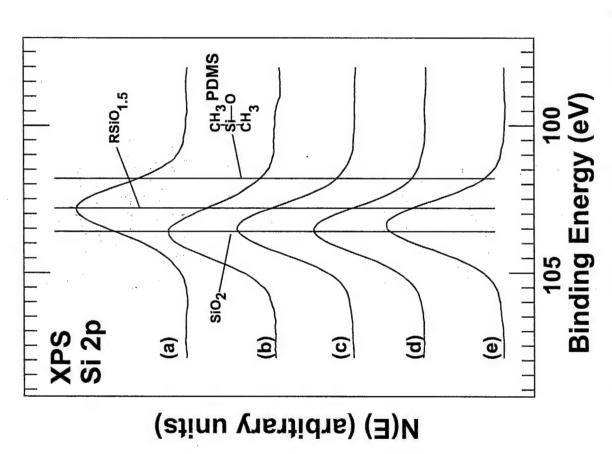




vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the 4.75-hr air exposure following the 63-hr AO exposure.



High Resolution C 1s and O 1s spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

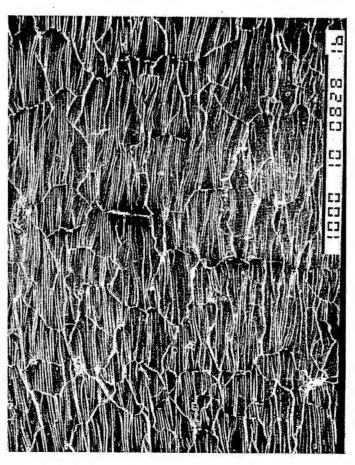


High Resolution Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.



SEM of POSS-Siloxane Copolymer







copolymer surfaces. The simulated LEO exposure "healed" the micro-cracks present initially in the POSS-siloxane sample. SEM of (a) unexposed and (b) exposed POSS-siloxane



POSS-Polyurethane



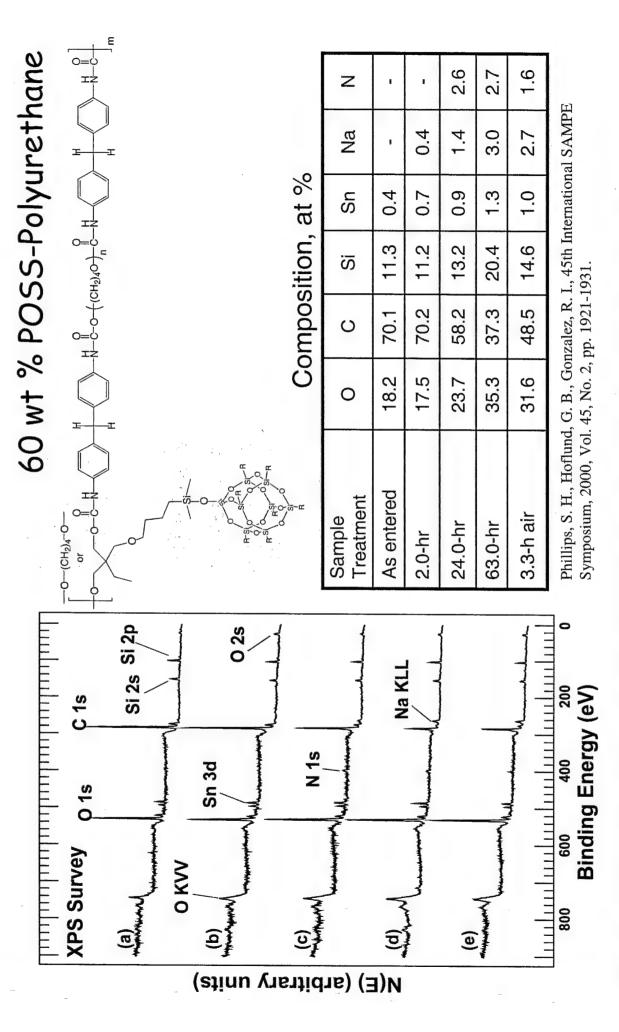
R = cyclopentyl POSS-TMP diol

Et₃N/DBTDL PTMG (M_n=2000) 1,4-butanediol

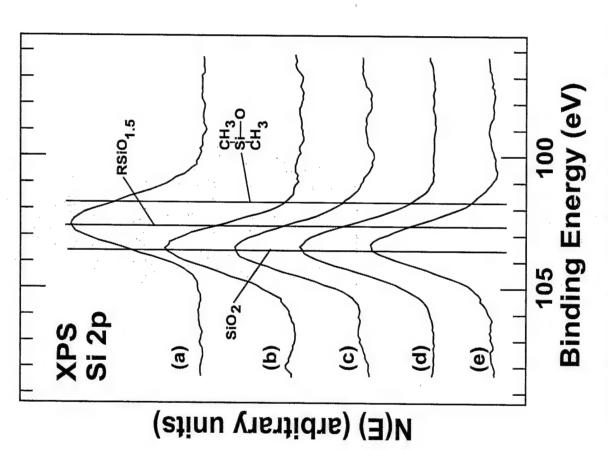
$$\begin{array}{c|c} & & & & \\ & &$$

Fu, B.X., et al. High Performance Polymers, 2000. 12(4): p. 565-571.

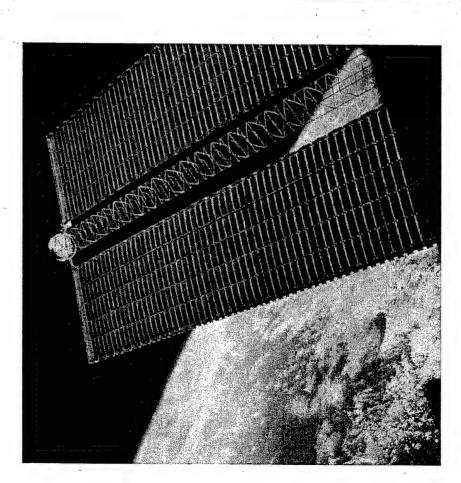
Fu, B.X., et al. Polymer, 2001. 42(2): p. 599-611.



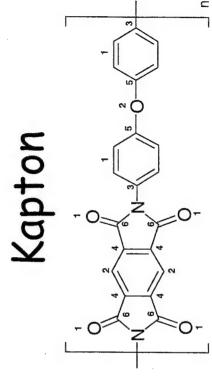
XPS Survey Spectra from a 60 wt% POSS-PU (a) after insertion into the vacuum system, (b) 2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 3.3-hr air exposure following the 63-hr exposure. after a



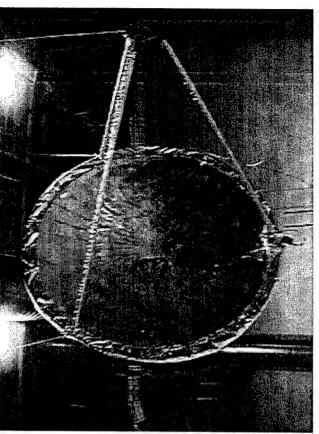
2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) High Resolution Si 2p spectra from a 60 wt% POSS-PU (a) after insertion into the vacuum 3.3-hr air exposure following the 63-hr exposure. system, (b) after a



Solar arrays Space inflatable structures



3.0 x 10-24 cm³/atom

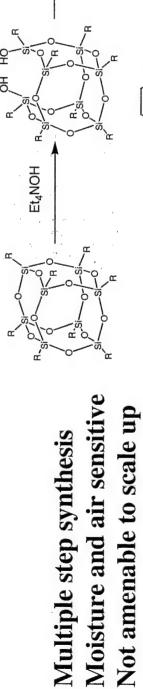


Superior optical properties, low solar absorptance, high thermal reflectance

Excellent mechanical thermal properties

First POSS-Aniline Synthesis



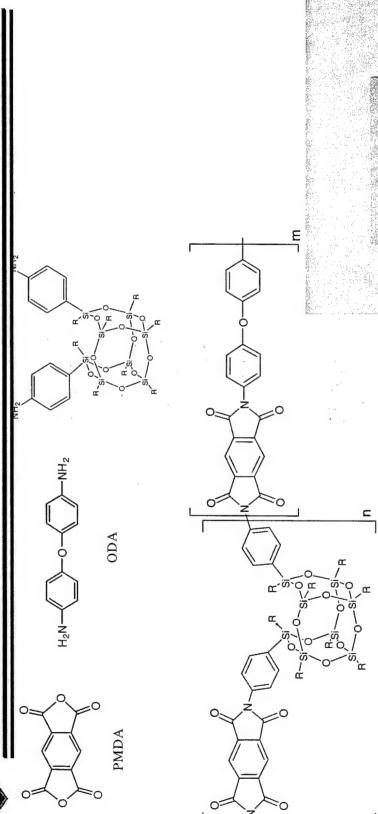


HBF₄/BF₃

Yet Critical for Development of POSS-polyimides!!!

POSS-Kapton Polyimides



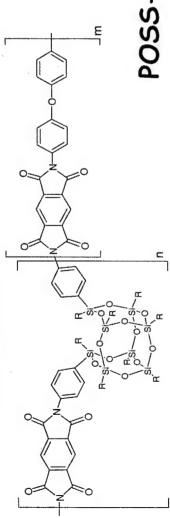


transparent films

• no aggregates formed

POSS High Performance Polyimides

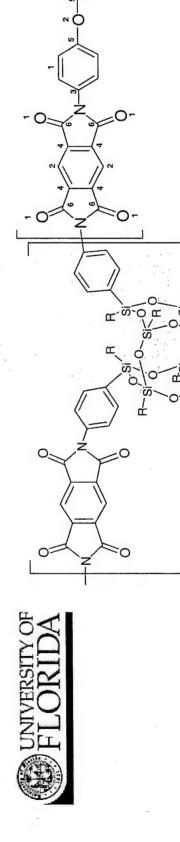


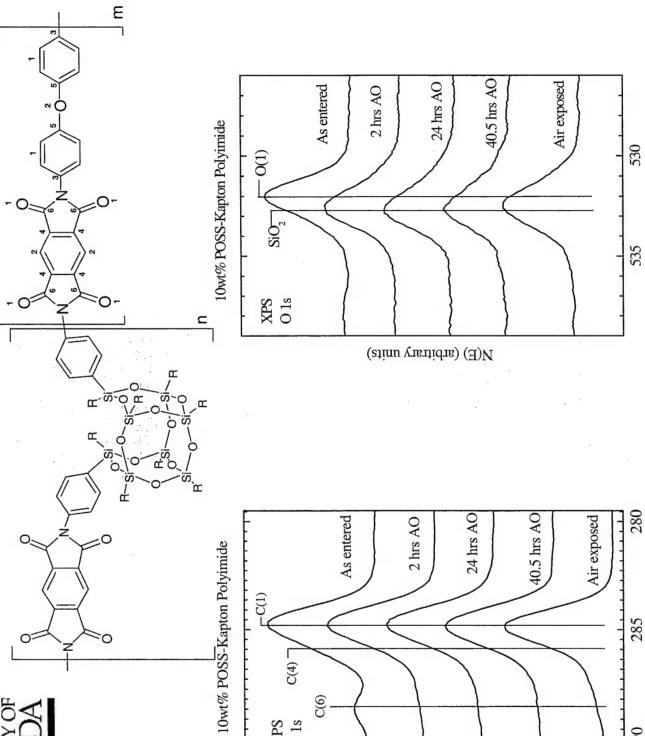


POSS-Kapton polyimide

POSS processable ether-imide

POSS-Fluorinated colorless polyimide





C(4)

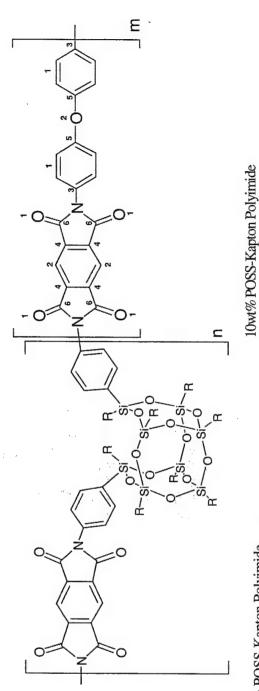
N(E) (arbitrary units)

Binding Energy (eV)

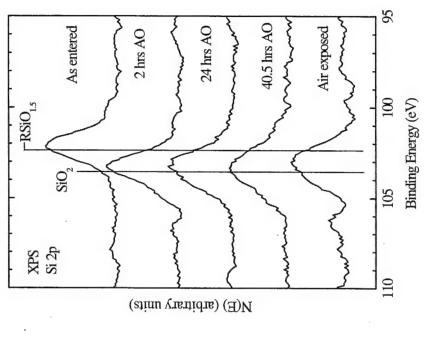
Binding Energy (eV)

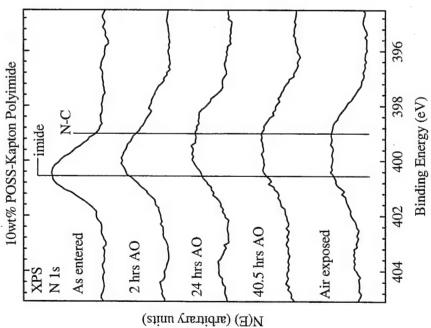
290







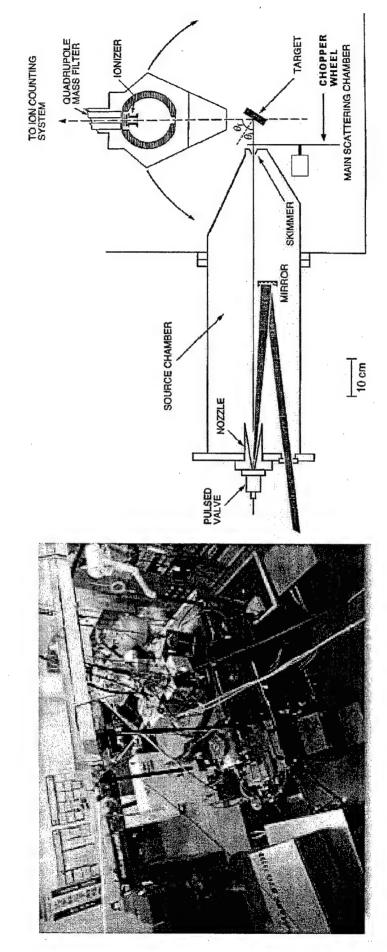






Beam-Surface Scattering/Atomic Oxygen Test Facility







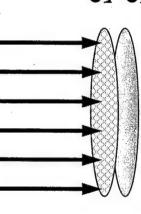




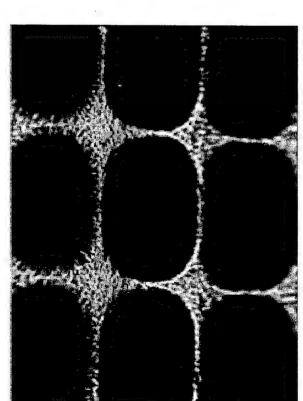
Surface Topographical Analysis/Profilometry



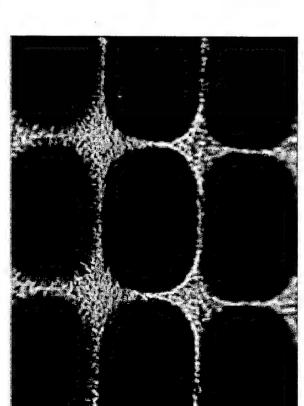
Hyperthermal AO Beam



Sample Screen



Kapton 10 wt% POSS

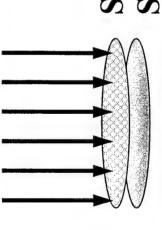


Kapton H

Fotal AO fluence of 2.62 x 10²⁰ atoms/cm² (~ 3 Days in LEO O-Atom etching experiment of POSS-Kapton polyimides





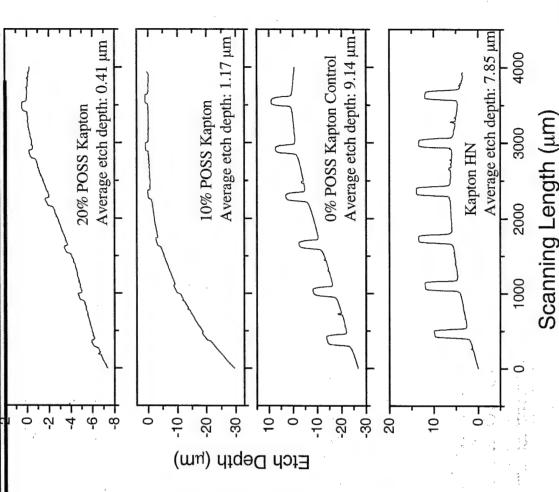


Screen

Sample

20 wt% POSS in Kapton results in over 20 time improvement in erosion resistance.

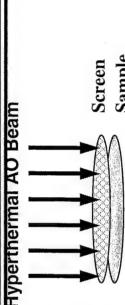


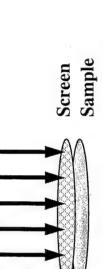




Total AO fluence of 8.47×10^{20} atoms cm⁻² (100,000 pluses) O-Atom Etching Experiment (~10 DAYS IN LEO)







Kapton H Standard

Average etch depth: **25.4** μ m Scanning Length (mm) 30 20 10 0 Average etch depth: 2.2 µm Kapton 10 wt% POSS Etch Depth (µm) 305

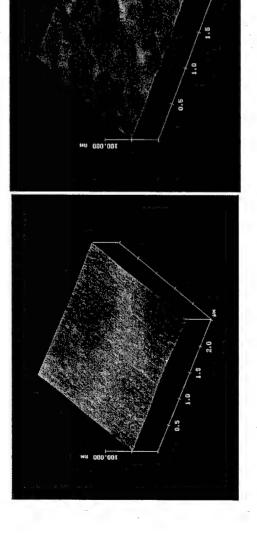
Significantly improved oxidation resistance due to a rapidly formed ceramiclike, passivating and self-healing silica layer preventing further degradation of underlying virgin polymer.





AFM Images of Unexposed POSS Polyimide Films





10% POSS

rms roughness: 1.03 nm

rms roughness:

1.09 nm

9% POSS

20% POSS

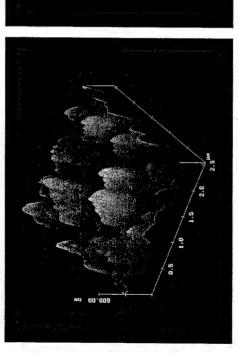
rms roughness: 1.55 nm



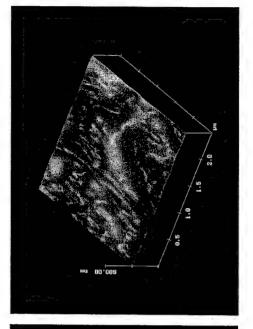


AFM Images of Exposed POSS Polyimide Films 100,000 Pulses of Hyperthermal (5 eV) AO Beam









0% POSS

rms roughness: 102 nm

10% POSS

rms roughness: 17.7 nm

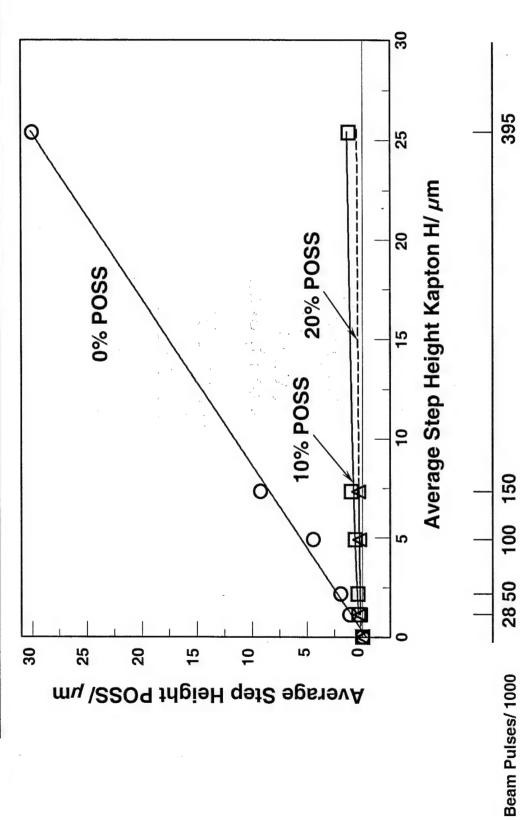
20% POSS

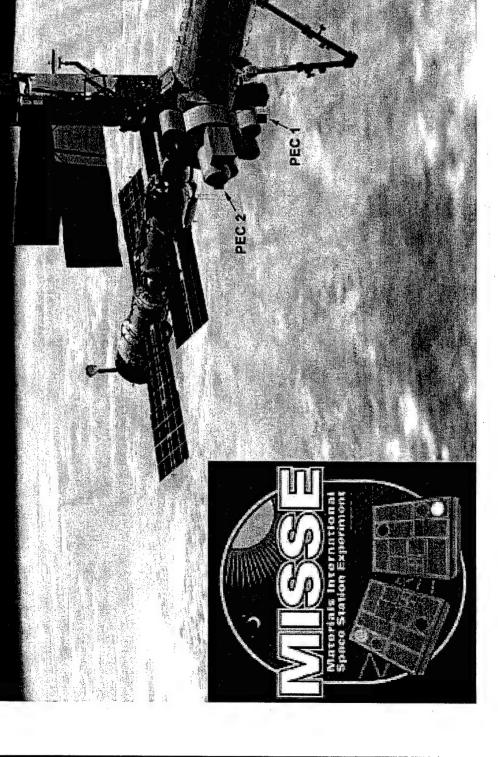
rms roughness: 6.75 nm



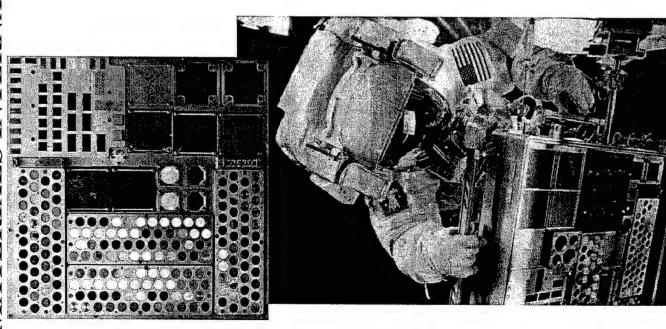
The state of the s

Erosion of POSS Polyimides by a Beam of Hyperthermal (5eV) O Atoms





MATERIALS INTERNATIONAL SPACE STATION EXPERIMENT



18 MONTH EXPOSURE TO LEO

POSS in Space

STS 105 Discovery and are deployed on the Int'l Space Station 16 August 2001

Footage courtesy of NASA



Tri-collaborative Effort for Proposed High-Risk, High-Payoff Program (Industry, Academia & Government)



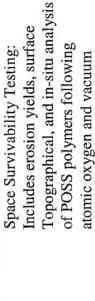


POSS-Aniline Synthesis. Scale up and Validation.











Michigan State University

ultraviolet radiation exposure

Thermal, mechanical, and dielectric Properties of POSS-polyimides.

POSS-Polymeric Materials Group Materials Application Branch AFRL, Edwards AFB

Efficient cost effective POSS-Aniline Monomer and POSS-Polyimide Synthesis.

Development, characterization, and testing of POSS-Polyimide composite materials with high temperature stability and space survivability.

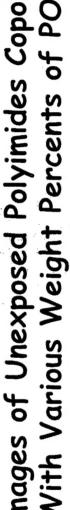


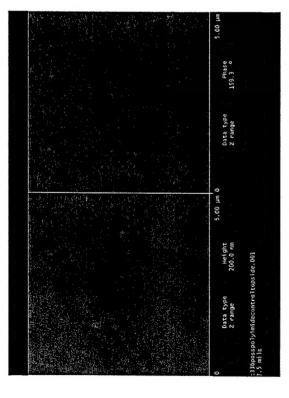
High Performance Polyimide Resins: NASA and Triton's co-developed Triton RTM PMR polyimides and POSS Incorporation in Triton's Phosphine Oxide Polyimides. Scale up and Validation.

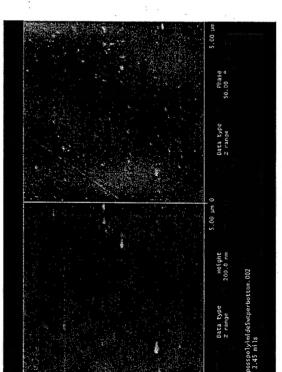


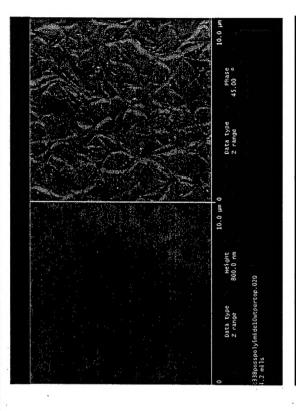
Includes simulated GEO exposure and mechanical property testing prior to Space Survivability Testing: and following exposure.

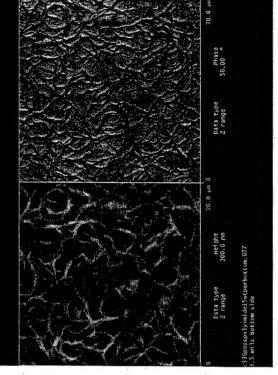
AFM Images of Unexposed Polyimides Copolymerized With Various Weight Percents of POSS











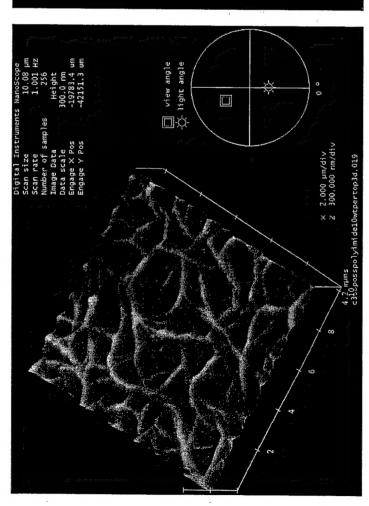


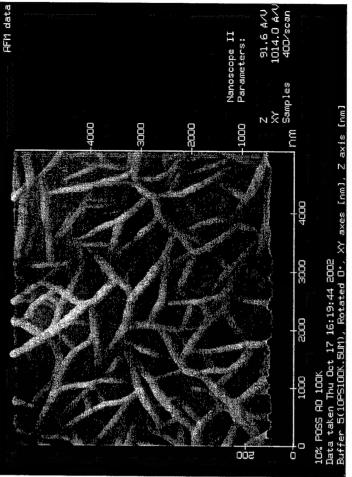
Three dimensional AFM Images 10 wt % POSS Polyimide Films











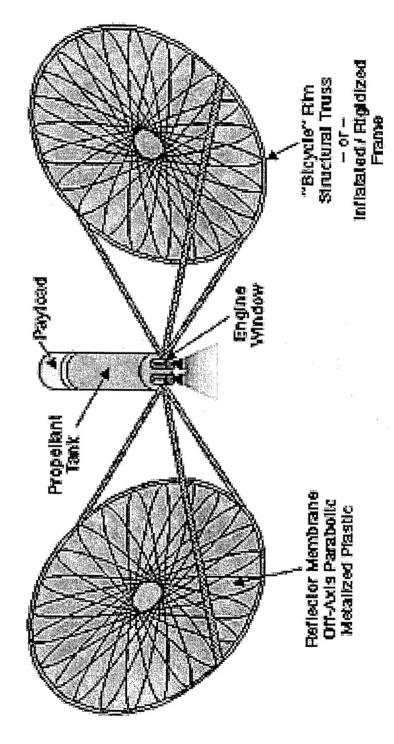
Unexposed

Exposed



Polyimides in Propulsion





propellant working fluid such as hydrogen. The collector mirrors are silvered balloon-like propellant.(Air force Phillips Laboratory and the NASA Marshall Spaceflight Center.) an open cavity on the side of the engine and focuses to a point to either directly heat the hydrogen propellant or heat a material such as graphite which then heats the hydrogen inflatable trusses. The light passes through a high temperature quartz window or into In a solar/laser thermal rocket, solar or laser light is collected and focused to heat a Inflatable structures or thin sheets of silvered plastic supported by lightweight

Polyimides in Propulsion



SRS Technologies'
(Huntsville, Alabama),
solar concentrators are made
almost entirely of castable,
clear polyimide film, a
lightweight material compared to
glass or metal optics.

